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Chemical modification of biomass residues during hydrothermal carbonization – What makes the difference, temperature or feedstock?

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ABSTRACT

Hydrothermal carbonization (HTC) of biomass may be a suitable technique to increase its carbon sequestration potential when applied to soils. However, the properties of end products of HTC (hydrochars) could be significantly influenced by feedstock source and temperature during the carbonization process. This study focused on chemical modification of wheat straw, poplar wood and olive residues through HTC at different temperatures (180 °C, 210 °C and 230 °C). Besides general properties such as pH, electrical conductivity (EC), ash content, elemental composition and yield, we evaluated bulk chemical composition (^{13}C NMR) and contribution of specific compounds (lignin and black carbon). Moreover, the possible environmental risk of using hydrochars was assessed by determining their polycyclic aromatic hydrocarbon (PAH) and their dioxin contents. Our results showed that hydrochars were generally acidic with a pH value below 5. The highest EC (1710 μS/cm) and ash content (10.9%) were found in wheat straw derived hydrochars. Hydrochar yields and C recovery decreased with increasing temperature to about 50% and 75%, respectively for all feedstocks at 230 °C. N recovery increased with increasing temperature but N content of feedstock is more important. H/C and O/C ratios showed a linear decrease with increasing production temperature for all feedstocks. O–alkyl C decreased while alkyl C and aromatic C increased with increasing temperature and no significant feedstock dependence could be observed. Carboxyl C was not influenced by feedstock and temperature. Lignin content decreased with increasing temperature, while its oxidation degree and the content of black carbon and PAH contents increased. We conclude that transformation of biomass was most advanced at 230 °C only. Feedstock did not significantly influence the chemical composition of the hydrochars apart from N content and recovery. Instead, HTC temperature is the main driver determining the chemical composition of hydrochars. Environmental risk of investigated hydrochars is low with respect to PAH and dioxin contents. Despite the advanced biomass transformation during the HTC process at 230 °C, chemical properties indicated that the end product might have a less stable structure than pyrochar. Considering the higher hydrochar yields and C and N recoveries, its C and N sequestration potential in soil could have some advantages over hydrochars but this still remains to be evaluated.

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1. Introduction

Increase of soil carbon sequestration following biochar application to soils has been proposed as a solution to counteract rising atmospheric CO_2 concentrations and improve soil quality (Glaser et al., 2002; Marris, 2006). Usually, biochar is produced by pyrolysis of biomass (pyrochar). In recent years an alternative procedure (hydrothermal carbonization, HTC) has been developed to transform labile biomass into a more stable end product (hydrochar). HTC is a process of heating biomass together with water at a temperature between 180 °C and 250 °C in a pressure vessel for several hours (Libra et al., 2011). Pressure cannot be controlled and depends on the steam pressure of water and gas development during feedstock decomposition. A clear scientific definition of the products of hydrothermal carbonization does not exist. From a chemical point of view, hydrochars are similar to brown coal, due to their low degree of carbonization and therewith a low degree of aromaticity and high proportion of functional groups on its surface (Libra et al., 2011; Schimmelpfennig and Glaser, 2012). The process of hydrothermal carbonization resembles a torrefaction process which involves heating at 200–300 °C at slow heating rates

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(<50 °C/min) under an anoxic atmosphere (Amonette and Joseph, 2009). Therefore, the chemical properties of hydrochars are not comparable to pyrochars because of different carbonization processes and thermochemical reactions (Cao et al., 2010). For instance, pyrochars are dominated by aromatics and hydrochars by aliphatics (Titirici et al., 2008). The chemical conversion of biomass during the HTC process is a series of hydrolysis, condensation, decarboxylation and dehydration reactions (Titirici et al., 2007; Sevilla and Fuertes, 2009a,b; Funke and Ziegler, 2010). However, knowledge about the formation of aromatic and potentially toxic compounds during hydrothermal carbonization at different temperature stages from various feedstocks is highly complex and not fully understood.

Therefore, the purpose of this study was to evaluate whether feedstock or temperature is the dominant driver for the chemical composition of hydrochars. For this purpose, nine different hydrochars were produced from three different feedstocks (poplar wood, olive residues and wheat straw) at three different temperatures (180 °C, 210 °C and 230 °C). The reactor used in this study reaches a maximum temperature of 230 °C (Section 2.2). Below a temperature of 180 °C, essentially no chemical modification of biomass occurs. Therefore, the lowest and highest possible temperatures (from a technical point of view) were chosen. The intermediate temperature of 210 °C was used for gradual traceability of the chemical conversion of biomass during the hydrothermal carbonization process.

The objectives of the present study were (i) to quantify the main influencing factors (e.g. production temperature and feedstock) regarding the chemical properties of hydrochars and (ii) to evaluate the stability of hydrochars and its contribution to long term C sequestration in soils based on its elemental and chemical composition and (iii) to evaluate the risk of hydrochars as a possible source of organic pollutants.

2. Materials and methods

2.1. Feedstocks

Chars were obtained from three different forestry and agriculture by-product feedstocks: Poplar wood chips, solid olive residues and wheat straw. Poplar (*Populus* spp. L.) wood chips, as a fast growing, renewable raw material, were obtained from dedicated short rotation forestry in northern Italy (Po Valley – Gadesco Pieve Delmona (CR), Lombardy, 45°10′13″N, 10°06′01″E). The age of the forestry at harvesting was 5 years. Solid olive residues are by-products of the olive milling process and often used as soil manure. The wet material is suitable for hydrothermal carbonization without energy intensive drying for the process as needed for pyrolysis. Olive residues were produced in Tuscany (San Giovanni Valdarno (AR), Tuscany) by means of a continuous oil extraction process with two-phase decanters. Wheat straw (*Triticum* spp. L.) was produced close to the poplar (Po Valley – Gadesco Pieve Delmona (CR), Lombardy – 45°08′59″N, 10°08′28″E) as by-product of grain and therefore available in large quantities; after harvesting, straw was chopped and briquetted. All feedstock materials were free of contaminants such as stones, metal, rubber, plastic, pollutant compounds and other foreign bodies, being direct products or by-products of agriculture.

2.2. Preparation of hydrochars

Hydrochars out of poplar wood, olive residues and wheat straw were produced at 180 °C, 210 °C and 230 °C and a corresponding average pressure of 10, 20 and 30 MPa, respectively. The producer Artec Biotechnology GmbH (Bad Königshofen, Germany) used the reactor b.coal 2.0 for laboratory scale production. The reactor is a stainless steel autoclave, holds a volume of 1.8 l and reaches a maximum temperature of 230 °C and a maximum pressure of 40 bar (burst pressure is 55 bar). About 300 g of each type of biomass was loaded into the pressure vessel and mixed with 1000 ml water together with citric acid as catalyst. The temperature was raised to 180 °C, 210 °C or 230 °C and the reactor was kept at temperature for 8 h. After HTC, all hydrochars were separated from slurry. The solid hydrochars were dried at 40 °C in a drying oven for 48 h. Samples were ground with an oscillating disk mill.

2.3. Chemical characterization

2.3.1. pH value

For measuring pH and electrical conductivity (EC) of hydrochars and feedstocks, suspensions with 0.01 mol/l $CaCl_2$ and distilled H_2O (1:5) were prepared. The mixtures were shaken for 1 h on a low speed shaker at room temperature. After sedimentation of hydrochar material for another hour, EC and pH were determined in the supernatant.

2.3.2. Ash content

For determining the ash content, 0.5–2 g of sample were weighed into pre-heated (500 °C) porcelain crucibles. After 4 h drying at 105 °C in a drying oven, the samples were re-weighed after cooling in a desiccator. Ashing occurred at a temperature of 550 °C for 8 h in a muffle furnace. The temperature increase was slow (3 °C/min) to prevent the formation of open fire due to the high organic content of the samples. After cooling in a desiccator, samples were weighed again. Determination of the ash content was calculated as mass loss on an oven dry basis.

2.3.3. Elemental composition

Total C, N, S and H contents were determined at the Institute of chemistry of the Martin-Luther-University in Halle (Germany) using a “vario EL” analyser by Elementar GmbH (Hanau, Germany). The total O content was measured by using a EURO EA Elemental Analyser (EuroVector, Hekatech, Germany) at the Soil Biogeochemistry Department of the Martin-Luther-University in Halle (Germany).

2.3.4. ^{13}C NMR

Solid state ^{13}C NMR spectra were recorded on a Bruker DSX 200 NMR spectrometer using cross polarization magic angle spinning (CPMAS) (Schaefer and Stejskal, 1976). A spinning speed of 6.8 kHz and a contact time of 1 ms were applied. A ramped 1H pulse starting at 100% power and decreasing until 50% was used during contact time to avoid Hartmann–Hahn mismatches (Peersen et al., 1993). A pulse delay of 2 s was chosen for all samples. Spectra were integrated by the integration routing of the spectrometer after phasing and baseline correction. We chose a line broadening of 50 Hz.

2.3.5. Lignin

Lignin content of feedstock and hydrochars was analyzed after CuO oxidation (Hedges and Ertel, 1982) as modified by Kögel and Bochter (1985). Briefly, 50 mg of sample were oxidized with 250 mg CuO and 2 M NaOH at 172 °C under N_2 for 2 h. After purification of the CuO oxidation products, lignin monomers were quantified gas chromatographically after silylation with BSTFA (N,O-bis(trimethylsilyl) trifluoro-acetamide, Fluka) (Hedges and Ertel, 1982). The lignin oxidation products were separated and detected with a HP GC 6890 gas chromatograph, equipped with a SGE BPX-5 column (50 m length, 0.25 mm inner diameter, 0.32 μm coating) and a flame ionization detector. Samples were injected in split mode (1:10). The GC oven temperature was programmed at 100 °C for 2 min, then from 100 °C to 172 °C at 8 °C/min, from 172 to 184 °C at 4 °C/min, and from 184 to 300 °C at a rate of 10 °C/min.

CuO oxidation yields a suite of phenolic compounds, consisting of vanillyl (V), syringyl (S) and cinnamyl (C) units, deriving from coniferyl, syringyl and p-coumaryl units respectively, with aldehydic, ketonic and acidic side chains. The sum of phenolic oxidation products VSC is used as estimate of intact lignin structural units. The acid/aldehyde ratios of lignin units S and V usually increase with increasing degradation.

2.3.6. Black carbon

Black carbon content and composition was determined using benzenepolycarboxylic acids (BPCAs) as molecular markers (Glaser et al., 1998; Brodowski et al., 2005). Briefly 10 mg of ground hydrochar were weighed into a flask and hydrolyzed with 10 ml of 4 M trifluoroacetic acid (TFA) for 4 h at 105 °C. The hydrolyzate was filtered by using a Buchner funnel and glass fiber filters and rinsed three times with deionised water. The collected residue plus the part of the contaminated filter were transferred quantitatively into a quartz digestion tube. After adding 2 ml 65% HNO_3, the digestion tubes were heated at 170 °C for 8 h in a pressure digestion apparatus. After cooling, the solution was filtered into a 10 ml volumetric flask through an ashless cellulose filter. After purification using cation exchange resins (Dowex 50W, 200–400 mesh) the solutions were freeze dried. The freeze dried samples were transferred with 3 ml methanol into 3 ml reaction vials. The samples were evaporated under a stream of nitrogen and 100 μl of biphenylen-2,2-dicarboxylic acid (1 mg/ml) as second internal standard were added and also dried. The dried samples were derivatized with 125 μl pyridine and 125 μl N,O-bis(trimethylsilyl)-trifluoroacetamide for 120 min at 90 °C. After cooling, the samples were transferred into GC autosampler vials with glass inserts. Separation and quantification of individual BPCA was carried out with GC-FID using a HP5 column (30 m × 0.25 mm × 0.25 μm). GC operating conditions were as follows: Injector and detector temperatures 300 °C. Helium was used as carrier gas at 149 kPa (constant pressure) with a column flow of 1.72 ml/min. Temperature was set at 100 °C for 1.2 min, increased at 30.5 °C/min to 240 °C. This temperature was held for 4.2 min, then again increased at a rate of 40 °C to 300 °C and then held for 5 min. 1 μl of sample was injected at a split ratio of 1:25. The sum of individual BPCA is taken as the black carbon content after multiplication by 2.27, the conversion factor for charcoal as suggested by Glaser et al. (1998). Patterns of individual BPCA molecular markers were expressed by the proportion of B3CA (B3CA = $\sum$ hemimellitic, trimellitic, trimesic acids), B4CA (B4CA = $\sum$ pyromellitic, prehnitic, mellophanic acids), B5CA (B5CA = benzene pentacarboxylic acid) and B6CA (B6CA = mellitic acid).

2.3.7. Polycyclic aromatic hydrocarbons

The analytical determination of the PAHs was carried out by *Synlab Umweltinstitut GmbH* (Leipzig, Germany) according to German Industrial Norm for samples with low PAH content (DIN ISO 13877:1995–06). Twenty grams of ground sample were extracted two times with 300 ml of a mixture of acetone and cyclohexane (2:1) by shaking for 1 h followed by filtration. Acetone and polar compounds were removed by liquid–liquid extraction with H_2O. A 10 ml aliquot of the cyclohexane extract was further purified by filtration over a column containing 2 g of deactivated Al_2O_3 (11 g water plus 89 g Al_2O_3) and 1 cm of dried Na_2SO_4 on top. PAHs were eluted with 8 ml cyclohexane and 0.8 ml acetonitrile was added. Subsequently, the solution was dried under a gentle N_2 stream to a volume of 0.8 ml. Finally, 10 μl of 6-methlychrysene were added as internal standard and PAHs were measured using a HPLC–DAD. External standards and control samples were used for quality control.

2.3.8. Polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs)

This analysis was carried out on selected hydrochar samples by Wesseling Laboratorien GmbH (Landsberg, Germany). For the determination of polychlorinated dibenzodioxins (PCCDs) the German Industrial Norm (DIN 38414-24) was used. Twenty grams of the freeze dried and ground sample were spiked with 50 μl of an internal standard, a solution of ^{13}C labeled PCDD and PCDF in toluene. In a Soxhlet extractor, the sample was extracted with 450 ml toluene. The purification of the concentrated extract (10 ml) occurred in several steps. First it was conditioned in a separating column with sulfuric acid/sodium hydrate followed by an Al_2O_3 column, a silver nitrate/silica gel column and at last the gel permeation chromatography. A 0.5 ml sample aliquot was measured using a GC–HRMS in selected ion monitoring mode.

2.4. Statistics

The statistical software package SPSS Statistics 17.0 for Windows was used for statistics. The Kolmogorov–Smirnov test was used for testing data on normal distribution. Statistical differences among means were tested using ANOVA. Tukey HSD post hoc test was applied for normally distributed data to compare means. The nonparametric Mann–Whitney *U* test was applied when normal distribution could not be achieved by logarithmic transformation. Microsoft Excel was used for graphical representation of the dataset. Significance levels were defined as highly significant ($p \leqslant 0.01$, **), significant ($0.01 < p < 0.05$), and not significant ($p > 0.05$).

3. Results and discussion

3.1. General properties

The basic characterization of the feedstocks and hydrochars are given in Table 1. The pH values ($CaCl_2$) of the hydrochars were acid, ranging from 2.3–4.9. The EC of the hydrochars varied from 752–1710 μS/cm indicating a high salinity. The highest EC value was found in the wheat straw hydrochar produced at 210 °C and 230 °C. Increasing pH and EC values with increasing production temperature could not be observed, as reported by Singh et al. (2010) and Kloss et al. (2011) for pyrochars obtained by pyrolysis at different temperature.

Increasing the carbonization temperature from 180–230 °C increased the ash content of all three feedstocks. The ash content (Table 1) of the wheat straw derived hydrochar was highest and varied with temperature from 5.8–10.9%. The ash content of the olive residue and poplar wood hydrochars was much lower (2.1–3.4%), due to the woody nature of the feedstocks.

3.2. Elemental composition

The total C and N contents (Table 1) of all feedstocks increased with increasing carbonization temperature. In general, olive residues have the highest total C and N contents in feedstock (498.8 C g/kg and 7.4 N g/kg) and carbonized hydrochars (579.9–675.6 C g/kg and 8.7–13.7 N g/kg) compared to wheat straw and poplar. Total C contents of our hydrochars are lower than those reported by Libra et al. (2011). Char yield showed a strong decrease with temperature from 75–90% to about 50% at 230 °C. Interestingly, total N concentration and N recovery increased during hydrothermal carbonization making this technique interesting for efficient N retention within ecosystems.

Table 1
General properties of feedstocks and hydrochars produced at 180 °C, 210 °C and 230 °C.

Sample	°C	pH ($CaCl_2$)	pH (H_2O)	EC (μS/cm)	Ash (%)	C (g/kg)	N (g kg^1)	C/N	Yield[a] (%)	C recovered (%)	N recovered (%)
Poplar wood	Feedstock	5.8	6.6	219	3.7	450.2	9.7	46.5	100.0	100.0	100.0
	180	4.8	4.9	752	2.2	509.6	5.3	85.9	89.9	101.8	49.5
	210	4.9	4.6	765	2.7	579.0	7.9	69.9	66.9	86.0	54.3
	230	4.4	4.9	638	3.4	659.0	13.5	69.5	51.9	76.0	72.0
Olive residues	Feedstock	6.5	7.1	471	16.4		7.4	65.8	100.0	100.0	100.0
	180	4.3	4.3	966	2.2	579.9	8.7	78.0	75.4	89.3	88.3
	210	4.4	4.4	975	2.1	642.7	10.2	73.5	63.3	83.1	87.3
	230	4.3	4.3	951	2.6	675.6	13.7	57.7	49.0	67.6	90.4
Wheat straw	Feedstock	5.5	6.8	989	6.7	431.1	4.5	95.8	100.0	100.0	
	180	4.2	4.3	910	5.8	494.8	6.7	111.2	80.1	91.9	119.6
	210	4.3	2.8	1710	9.4	555.8	9.3	85.7	54.6	70.4	112.5
	230	2.3	2.8	1497	10.9	602.3	10.1	57.1	53.7	75.0	120.5

[a] Yield expressed as g product/100 g raw material.

The C/N ratio of poplar wood, olive residues and wheat straw was 46.5, 65.8 and 170.5, respectively (Table 1). The C/N ratio increased at 180 °C but substantially decreased with increasing carbonization. The C/N ratio of the wheat straw hydrochar strongly decreased to 111.2 at 180 °C compared to the feedstock. In comparison to the other hydrochars in the sample set, the difference of the C/N ratio of wheat straw hyrochar produced at 180 °C and 230 °C is highest. Taking a C/N ratio of <30 as predictor for N mineralization and C/N ratios > 30 as predictor for initial net immobilization of N (Stevenson and Cole, 1999), none of the hydrochars leads to an increased N availability in soil after application. However, as already mentioned above, decreasing C/N ratio and increasing N recovery with increasing HTC temperature is favorable for N retention in hydrochars and needs further attention.

3.3. Elemental ratios

The van Krevelen diagram (Fig. 1) gives an indication on the carbonization process and thus, on hydrochar properties like polarity and aromaticity of the investigated hydrochars. As expected, feedstocks have higher O/C and H/C ratios compared to hydrochars. The O/C and H/C ratios of all carbonized feedstocks decreased with increasing production temperature, indicating a loss of oxygen and hydrogen during progressing carbonization. Poplar wood hydrochars have the highest decrease of H/C and O/C ratio from 1.38 to 0.98 (29%) and 0.58 to 0.26 (56%), respectively. In contrast, the H/C ratio of the olive residues temperature set decreased only from 1.31 to 1.10 (16%) and the O/C ratio from 0.38 to 0. 0.20 (47%) through thermal alteration. The H/C ratio of the wheat straw derived hydrochar declined around 16% (from 1.31 to 1.10) whereas the O/C ratio was reduced by 47% (from 0.55 to 0.28). A decreasing H/C ratio indicates demethylation (loss of CH_3) and a decreasing O/C ration indicates decarboxylation (loss of CO_2) which forms products more rich in carbon (van Krevelen, 1961). Polar functional groups, existing in feedstock and low carbonized materials are indicated through a higher atomic O/C ratio. In other words, a high O/C ratio indicates a low carbonization grade and hence most probably a lower stability against degradation in soils but also a higher reactivity. According to previous studies on pyrochars (e.g. Kuhlbusch and Crutzen, 1995; Hammes et al., 2006), an H/C ratio of $\leqslant 0.3$ indicates a highly condensed aromatic ring system, whereas an H/C ratio of $\geqslant 0.7$ represents a non-condensed aromatic ring system. Kuhlbusch and Crutzen (1995) suggest an H/C ratio of $\leqslant 0.2$ as representative threshold for black carbon. Desirable O/C and H/C ratios of biochars suitable for C sequestration in soils are $\leqslant 0.4$ and 0.6, respectively (Schimmelpfennig and Glaser, 2012). In our study, O/C ratio of POP180, POP210 and WS180 are >0.4 whereas none of the hydrochars exhibited an H/C ratio $\leqslant$ 0.6. However, when compared to the initial feedstock, hydrochars seemed to have experienced some kind of transformation. Therefore, they might have gained in stability towards microbial decay. However, at the same time, char yield greatly decreased

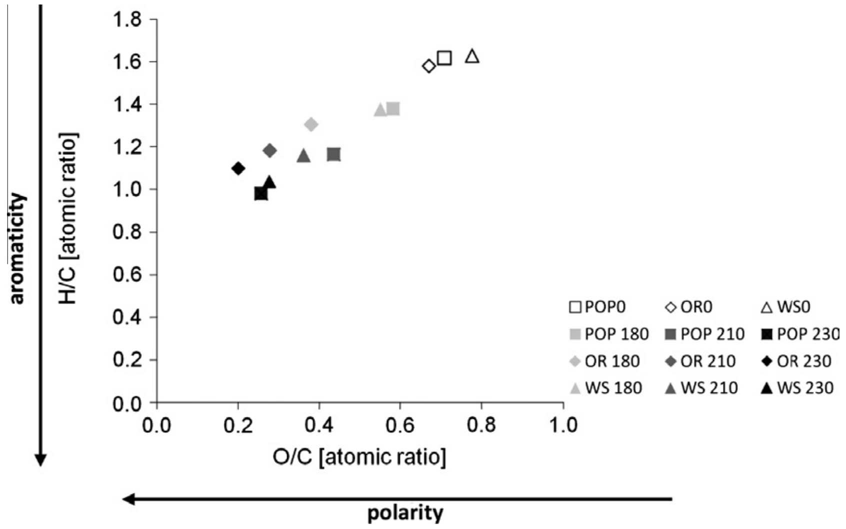

Fig. 1. O/C and H/C ratios in a 'van Krevelen diagram'. Squares, diamonds and triangles indicate poplar (POP), olive oil residues (ORs) and wheat straw (WS), respectively. Numbers indicate temperature (°C) of hydrothermal carbonization.

(Table 1), being similar to pyrochars produced at 300–350 °C and higher than pyrochars produced at temperatures >350 °C (Glaser et al., 2002). This should be considered when evaluating a possible stability gain. Further chemical characterization is needed to evaluate if lower H/C and O/C ratios are indicative of aromatization of the material. The high O/C ratio of hydrochars could indicate the presence of more hydroxyl, carboxyl and carbonyl groups, which leads to the assumption, that hydrochars have higher cation exchange capacity compared with pyrochars.

3.4. ^{13}C NMR

Solid state ^{13}C NMR spectra of feedstocks and hydrochars at different temperature are shown in Fig. 2. All three feedstocks are characterized by a high contribution of O–alkyl C at 45–110 ppm, most probably derived from polysaccharides (Kögel-Knabner, 1997). Additionally, signals derived from methoxyl C of lignin are present at 56 ppm. Signal intensity in the O–alkyl C region of the spectra decreased linearly with increasing temperature from 70–80% in feedstock to 20–30% in hydrochar produced at 230 °C (Fig. 2, Table 2). Moreover, small signals in feedstocks can be observed in the aryl and alkyl regions of the spectra at 110–160 ppm and 0–45 ppm, respectively. The signals at 119 and 150 ppm may be assigned to lignin compounds and represent protonated, O-substituted aromatic C and methoxyl C (Knicker et al., 1995). In the alkyl region of the spectra, signals at 30 ppm may originate from long chain aliphatic molecules such as cutin or suberin, whereas the signal at 20 ppm may be derived from short chain aliphatic structures (Golchin et al., 1998). Alkyl C and aryl C increased upon hydrothermal carbonization at higher temperatures. Aryl C increased from 11–14% to 41–45% of total signal intensity in feedstock and hydrochars produced at 230 °C, respectively (Table 2). Alkyl C contribution to total signal intensity increased from 5–10% in the feedstock to 20–30% in the 230 °C hydrochars (Table 2). Carboxyl C most likely assigned to organic acids as well as amide contribution (Skjemstad et al., 1996) had the lowest contribution to total signal intensity between 4% and 9%, which remained stable during hydrothermal carbonization. Thus, hydrothermal carbonization of wood as well as herbal biomass is characterized by a loss of polysaccharides and a gradual transformation of these compounds into aromatic as well as aliphatic structures (Table 2, Fig. 2). This is in sharp contrast to biochar production through pyrolysis reactions or during fire, which contains exclusively aromatic C structures (Schmidt and Noack, 2000; Knicker et al., 2008). Hydrothermal carbonization resembles more the coalification process, which shows the same kind of biomass alteration occurring through the influence of pressure and time (van Krevelen, 1961). Our data show a gradual increase of biomass alteration with increasing carbonization temperature being highest at 230 °C. At lower temperature, substantial amounts of polysaccharides are preserved, the resulting hydrochar being similar to low rank lignite, which can also show polysaccharide contribution (Hatcher et al., 1989). Regarding the ^{13}C NMR method used in this study, it has to mention that Fang et al. (2010) observed an underestimation of aromatic C in soil organic matter (SOM). However, the results of the black carbon and elemental composition underline the low content of aromatic C in hydrochars and therewith the results of ^{13}C NMR measurements.

Table 2
Relative contribution of alkyl C (0–45 ppm), O–alkyl C (45–110 ppm), aryl C (110–160 ppm), and carboxyl C (160–220 ppm) to total signal intensity of the solid state ^{13}C NMR spectra.

Sample	°C	Alkyl C	O–Alkyl C	Aryl C	Carboxyl C
Wheat straw	Feedstock	5	81	11	4
	180	11	61	23	5
	210	20	38	33	9
	230	31	20	41	8
Olive residues	Feedstock	10	71	14	4
	180	18	45	34	4
	210	24	29	37	9
	230	30	25	42	4
Poplar wood	Feedstock	6	78	13	2
	180	8	66	19	6
	210	17	46	34	4
	230	20	30	45	5

It is interesting to note that the nature of the feedstock influences the chemical composition of the hydrochars only to a minor and non-significant extent. In the following, we will examine the influence of feedstock as well as production temperature on specific compounds, which may be present in hydrochars.

3.5. Lignin

Lignin content of feedstocks ranged from 17–40 mg/g. Highest lignin content was recorded for poplar wood and wheat straw (Fig. 3). Lignin content generally decreased with increasing temperature of HTC (Fig. 3). Differences according to feedstock were

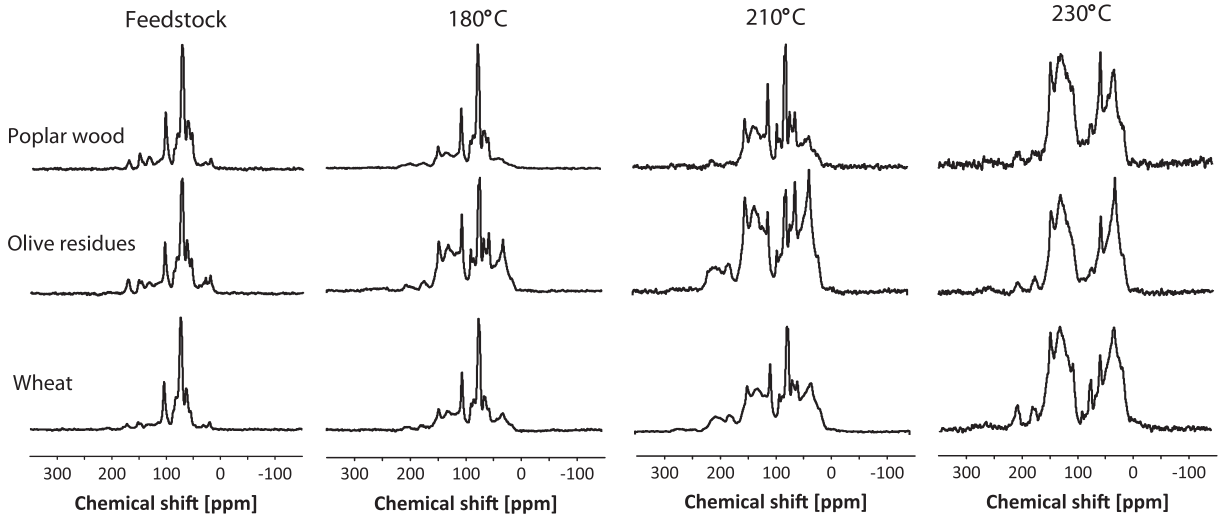

Fig. 2. Solid state ^{13}C NMR spectra of different feedstocks and hydrochars produced at three different temperatures.

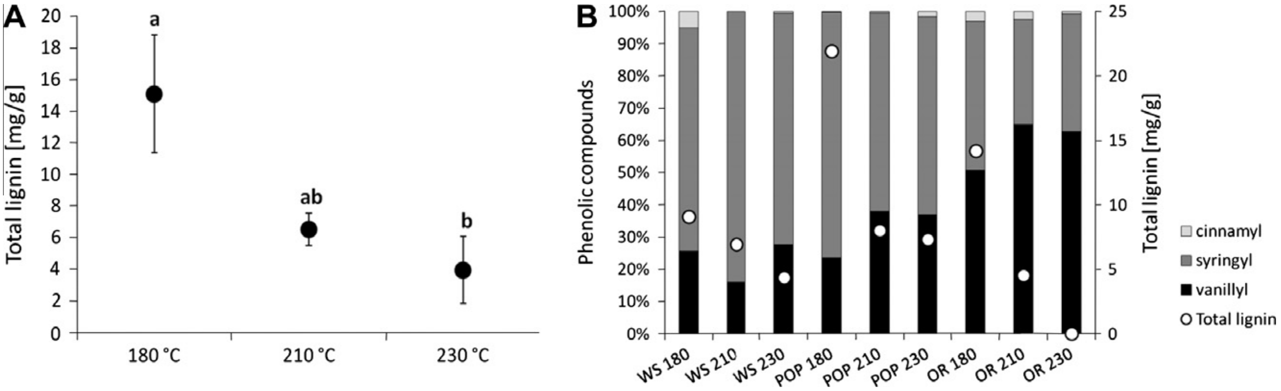

Fig. 3. CuO lignin content and relative contribution of individual lignin monomers of poplar (POP), olive oil residues (ORs) and wheat straw (WS) hydrochars. Numbers indicate temperature (°C) of hydrothermal carbonization.

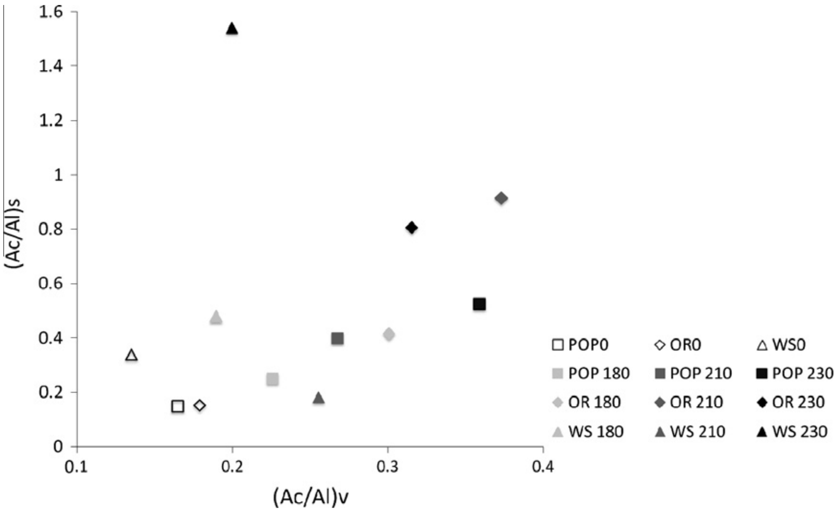

Fig. 4. Acid (Ac) to aldehyde (Al) ratio of syringyl (S) moieties of lignin of poplar (POP), olive oil residues (ORs) and wheat straw (WS) hydrochars. Numbers indicate temperature (°C) of hydrothermal carbonization.

noted. In particular, wheat straw showed the highest loss at the lowest carbonization temperature and complete lignin loss occurred for olive residues at the highest carbonization temperature (Fig. 3). The degree of lignin oxidation increased with increasing carbonization temperature (Fig. 4). The changes occurring due to HTC are similar to those occurring upon charring of biomass by the influence of fire, i.e. decreasing lignin content and increasing degree of oxidation with charring (Kuo et al., 2008; Nocentini et al., 2010). However, the lignin content of charred biomass was much lower and their acid/aldehyde ratio much higher than those of hydrochars. This may be explained by the less complete transformation into highly aromatic structures by HTC compared to heating during pyrolysis or natural fire. The strong heterogeneity of lignin biomarkers recorded for the hydrochars suggest that feedstock is dominating at low carbonization temperature (180 °C) while production temperature is the dominating variable controlling lignin content at carbonization temperatures >180 °C.

3.6. Black carbon

Mean black carbon (BC) concentrations significantly ($P < 0.05$) increased with increasing carbonization temperature from 18.4 to 92.4 g BC-C/kg total organic carbon (TOC) (Fig. 5A). Black carbon contents of the different feedstocks showed no significant ($P > 0.05$) differences between different feedstock within the same production process (Fig. 5B). They ranged from 10.8 to 25.9 BC g C/kg TOC for 180 °C, between 53.7 and 74.3 BC g C/kg TOC for 210 °C and between 80.4 and 104.7 BC g C/kg TOC for 230 °C. The increase of BC concentrations with increasing temperature was accompanied by an increase of C and N contents but a decrease of the C/N, H/C and O/C ratios (Table 1 and Fig. 1). This is in good agreement with the study of Schneider et al. (2010), showing similar results for charred wood.

Black carbon quality represented by individual BPCA molecular markers is presented in Fig. 5B. Differences of BPCA patterns between different feedstock with same charring temperature were only minor (Fig. 5B). BPCA patterns indicate changes in quality of the hydrochars with increasing charring temperature (Fig. 5). The proportions of less condensed BPCAs (B3CA and B4CA) of the same feedstocks decreased with increasing charring temperature whereas the proportions of highly condensed BPCAs (B5CA and B6CA) increased. This is in accordance with an increase of total BC contents (Fig. 5B) indicating both a higher degree of aromatization and a higher amount of condensed aromatic C with increasing carbonization temperature. Greatest changes of the BPCA distribution occurred between 180 °C and 210 °C while between 210 °C and 230 °C only small changes were observed (Fig. 5B). Interestingly, some hydrochars with similar BPCA patterns like WS210

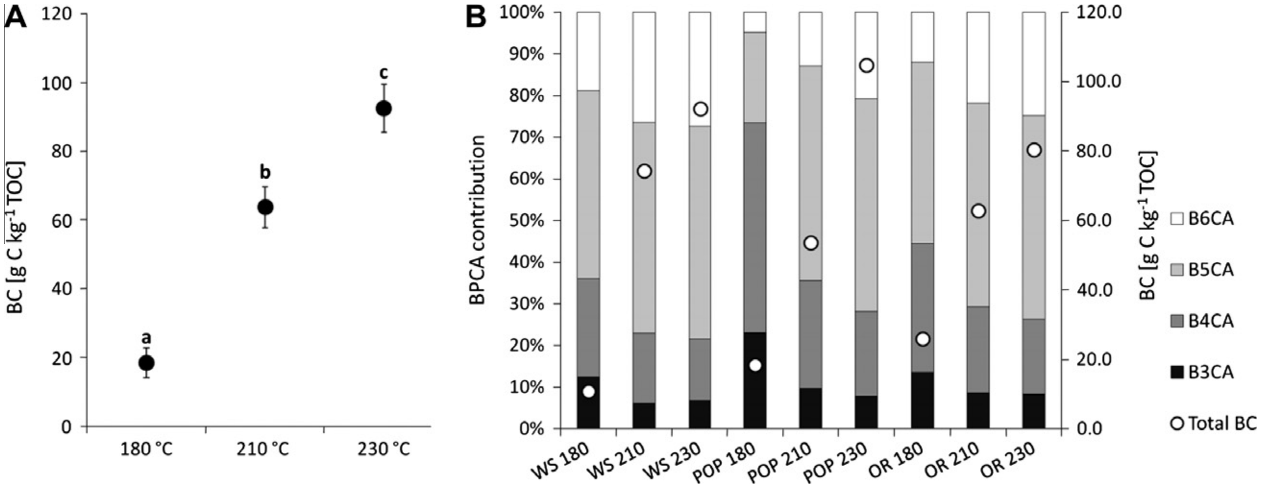

Fig. 5. Mean black carbon (BC) content (A) and relative contribution of individual benzenepolycarboxylic acids (BPCAs) and total BC content of individual hydrochars (white circles; B). Letters indicate significant differences (Tukey HSD test; $p < 0.05$; Error bars show SE). WS = wheat straw, POP = poplar wood, ORs = olive residues; 180, 210 and 230 indicates the production temperature.

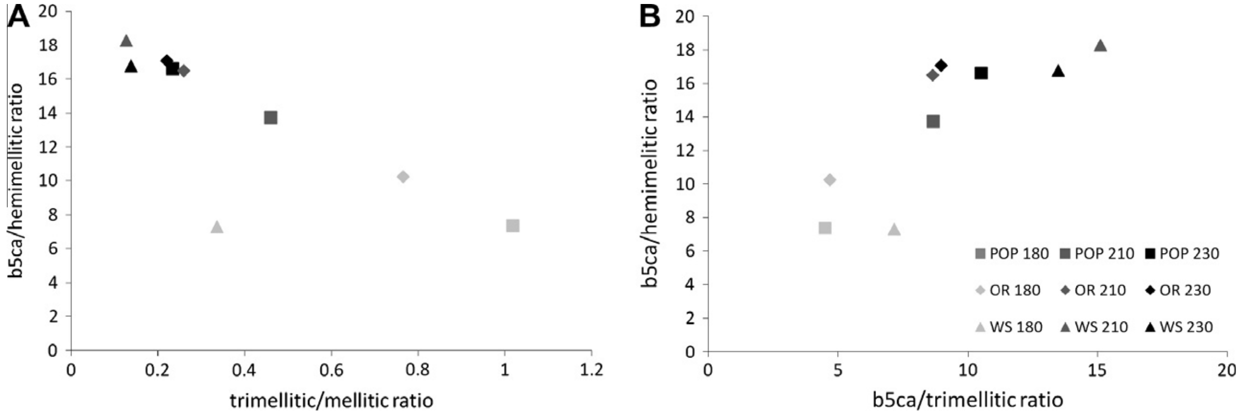

Fig. 6. BPCA ratios of hydrochars (B3CAs = benzene tricarboxylic acids; B5CA = benzene pentacarboxylic acid).

and WS230 or OR210 and OR230, had relatively high differences in total BC content averaging 17 g BC/kg TOC. In addition, poplar derived hydrochar had the highest increase of total BC content from 18.5 (POP180) to 104.7 (POP230) compared to hydrochars from wheat straw and olive residues. The proportion of B3CA and B4CA to B5CA and B6CA of POP180 is around 3:1 which turns into 1:3 for POP230. The proportion of the highly recalcitrant hexacarboxylic (B6CA) acid which is released from highly condensed, aromatic core of BC structures is comparable with pyrochars produced by pyrolysis at 300 °C (Glaser et al., 1998) but substantially lower compared to pyrochars produced at >500 °C (Schneider et al., 2010). A B6CA contribution of nearly 100% was observed at a charring temperature of 1000 °C (Schneider et al., 2010). Hence, the degree of aromatic condensation of hydrochars is comparatively low at least at low temperature, also reflected by the van Krevelen diagram. A high stability in soils could not be expected. Hydrochars produced at 230 °C are comparable to pyrochars produced at 300 °C.

BPCA ratios could act as an additional tool to estimate the quality of BC of different carbonized materials (Fig. 6). In this study, we took the trimellitic/mellitic and B5CA/hemimellitic acid ratios as well as the B5CA/trimellitic and B5CA/hemimellitic ratios as an estimate of BC quality. Fig. 6A shows a linear decrease of trimellitic/mellitic acid ratio and increase of B5CA/hemimellitic acid ratio for poplar wood and olive residue derived hydrochars with increasing charring temperature. Wheat straw derived hydrochars did not fit into this sequence because the trimellitic/mellitic acid ratio of WS210 was higher as those of WS230. The B5CA/trimellitic acid and B5CA/hemimellitic acid ratios showed a similar linear pattern (Fig. 6B) but in the opposite direction. Both ratios increased with increasing charring temperature. Both diagrams visualize once again the influence of different feedstocks on the intensity of transformation at 180 °C. However, the influence of feedstock decreased with increasing carbonization temperature.

3.7. Polycyclic aromatic hydrocarbons

Total PAH concentration of hydrochars is as important as their molecular weight distribution for their behavior in the environment like degradability, toxicity or solubility. However, knowledge about the bioavailability of PAHs and legal framework with regard to PAHs and other organic pollutants in hydrochars and biochars are still lacking. Additionally, the quantification of PAHs in hydrochars and biochars is method-dependent (Hilber et al., 2012). In our study, we used the analytical German DIN standard (Section 2.2) for soil PAHs to analyze the hydrochars. The results of the total mean PAH concentration and the percentage distribution regarding the number of aromatic rings of the investigated

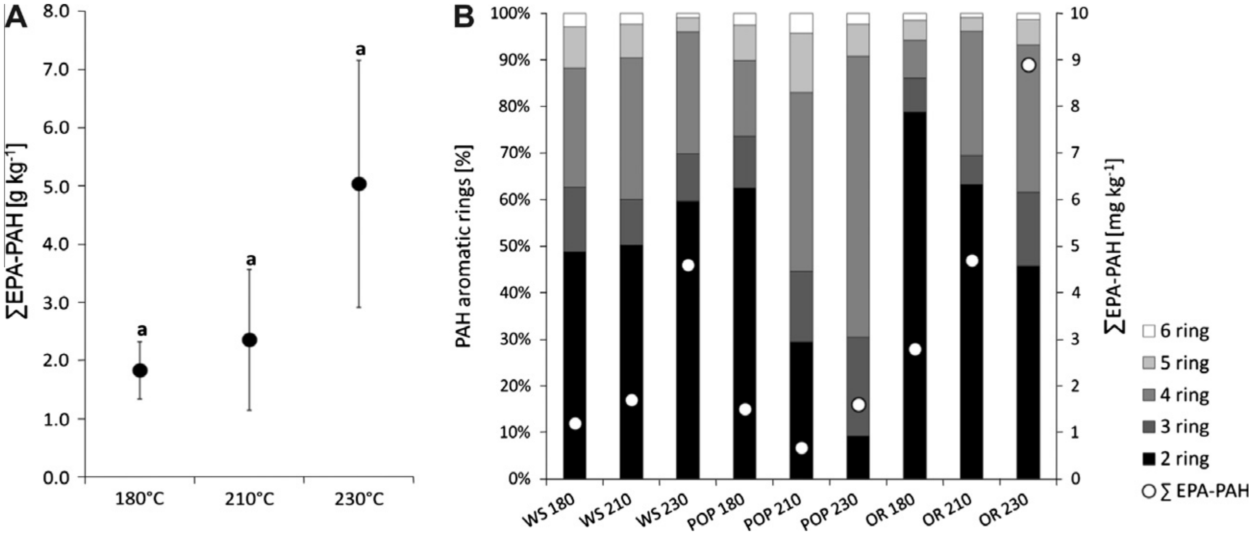

Fig. 7. Mean PAH concentration as function of HTC temperature (A), PAH concentration of individual samples (B) and relative contribution of individual PAHs (B). WS = wheat straw, POP = poplar wood, ORs = olive oil residues. Significant differences between the samples are shown by letters ($p < 0.05$; Mann–Withney *U* test; error bars show SE).

hydrochars are shown in Fig. 7. The total mean concentration of 16 EPA-PAH of the hydrochars showing no significant differences (Mann–Whitney *U* test, $p < 0.05$) but a consistent trend of increasing PAH amounts from 1.8 to 5.0 mg PAH/kg with increasing carbonization temperature could be observed. The high standard error (Fig. 7A) indicate a very heterogenic distribution of the PAH. No significant correlation was found between total PAH and total BC contents ($R = 0.38$).

Patterns of PAHs according to their molecular weight (Fig. 7B) showed heterogenic distribution with regard to feedstocks and charring temperature. However, the molecular composition of the wheat straw derived hydrochars showed negligible alteration with increasing charring temperature compared to hydrochars produced from poplar and olive residues. Nevertheless, total mean PAH content of WS230 strongly increased despite similar molecular pattern as WS180 and WS210. Molecules with two and four rings dominate the PAHs in wheat straw hydrochars of up to 59% and 31%, respectively. In all hydrochars, the proportion of 6-ring PAHs ranged between 1% and 4%, negligibly low. The wheat straw hydrochars showed a slight increase of the 2- and 5-ring PAHs with increasing temperature which is in contrast to poplar wood and olive residue hydrochars. Both sample sets showed a strong decrease of 2- ring PAHs from 62% (POP180) to 9% (POP230) and 78% (OR180) to 45% (OR230) with increasing charring temperature but an increase of 3- and 4-ring PAHs. Five ring PAHs showed no unequivocal pattern. The strongest change of PAH composition according to their molecular weight due to thermal alteration were recorded for poplar wood. Interestingly, total PAH contents for these samples ranged from 0.7–1.7 mg/kg and had no consistent trend with increasing temperature as was observed for wheat straw and olive residues. The most rapid increase of total PAH content with increasing charring temperature from 2.8 to 8.9 was observed for olive residues. This increase was accompanied by a decrease of 2-ring PAHs and an increase of 3- and 4-ring PAHs.

To evaluate the total PAH content of single hydrochars, a prescription and legal framework are urgently needed. Every European country, the USA and Australia have different legal arrangements for PAH threshold values. The limits are restricted with regard to biosolids, composts or soil but not for hydrochars or pyrochars. Using the German Bundes-Bodenschutz-und Altlastenverordnung (BBodSchV; German federal soil protection ordinance), most hydrochars are beyond the recommended limits of 3 or 10 mg/kg of total PAHs depending on the humus content ⩽8% or >8%. WS230 (4.6 mg/kg), OS210 (4.7 mg/kg) and OS230 (8.9 mg/kg) exceed the limit of 3 mg/kg if humus content is ⩽8%. In this study, hydrochars have the tendency of higher total PAH contents with increasing charring temperature which is in contrast to the results of Hale et al. (2012). They observed a decrease of total PAH concentration with increasing temperature. However, PAH evolution in pyrolyzed and hydrolyzed biomass is hardly comparable due to fundamental differences of the processes. Taking the standard limits for PAHs in biosolids in the EU ranging from 3–6 mg/kg (European Communities, 2001), WS230 and OR210 exceed the first and OR230 exceed the second limit. A further standard limit by the US-EPA for PAHs is 6 mg/kg. Regarding this regulation, OS230 is beyond this limit. However, when applied in limited quantity (<100 Mg/ha) PAH contribution is only 10% of these values to a maximum.

As already mentioned above, not only the total PAH content must be considered but also the contribution of individual PAHs. The pattern of single PAHs according their molecular weights (Fig. 7B) demonstrates clearly how heterogeneous hydrochars are produced in the same reactor but different temperatures and feedstock.

The molecular weight of PAHs plays an important role for the behavior of PAHs in the environment and their carcinogenic and mutagenic properties. Generally, steam pressure, water solubility and Henry's law constant of PAHs decreases with increasing molecular weight. PAHs with a higher molecular weight have a high sorption tendency and therefore a high potential of bioaccumulation. Studies regarding the release and bioavailability of PAHs from hydrochars and biochars in soils are urgently needed.

3.8. Polychlorinated dibenzodioxins (PCDDs)

The analysis of PCDD in poplar wood and olive residue hydrochars (both 230 °C) showed only low amounts of 8.1 ng TEQ/kg for the latter. Dioxin content of poplar hydrochar was under the detection limit (<5.98 ng TEQ/kg). These results are not surprising, because production temperature of hydrochars is <250 °C and dioxins are not produced at this temperature. The presence of chlorine and organic carbon during combustion processes at 300 °C and higher is the precondition for the synthesis of PCDDs. However, dioxins can already exist in feedstocks and carbonization temperature is too low to destroy them. Therefore, caution should be taken in the selection of feedstocks for hydrothermal carbonization which could be already contaminated with dioxins (e.g. sewage sludge).

4. Conclusions

Our results showed that chemical properties of hydrochars varied as a function of carbonization temperature and to a much lesser extent also to feedstock, especially at lower carbonization temperature. Analysis of elemental as well as bulk chemical composition showed that increasing temperature during the hydrothermal carbonization procedure leads to decreasing polarity and increasing aromaticity of hydrochars. Biomass transformation at increasing temperature is associated with decreasing lignin content, increasing degree of lignin oxidation as well as increasing amounts of highly condensed black carbon moieties. However, hydrothermal carbonization results in a product which is less aromatic and much less condensed than biochar produced during pyrolysis or fire. PAH content showed no significant but consistent temperature trend. Nevertheless, when viewing single total PAH contents and PAH patterns according their molecular weight, not only temperature but also feedstocks strongly influence the quality and quantity of hydrochars. Thus, feedstock characteristics are influencing the nature of hydrochar mainly for single compounds and at low temperatures. At carbonization temperature above 180 °C, material properties were nearly independent from feedstock highlighting a possible prediction of the environmental fate of hydrochars produced at defined conditions (especially temperature). However, the harmful and carcinogenic potential of polycyclic aromatic hydrocarbons (PAHs) and different legislation among countries can lead to possible source of organic pollutants if hydrochars are used irrationally in agrosystems outside a legislative framework. Therefore, further studies are needed to provide clues to the best management option in residue management and temperature regimes for hydrochar production.

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